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A STUDY OF THE IMPROVEMENT OF  
ELECTRICAL CONDUCTIVITY IN GLASS

by

WARREN E. DUNGAN

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NORTH CAROLINA STATE COLLEGE  
DEPARTMENT OF ENGINEERING RESEARCH  
SCHOOL OF ENGINEERING  
RALEIGH, N. C.

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# A STUDY OF THE IMPROVEMENT OF ELECTRICAL CONDUCTIVITY IN GLASS

## I. SUMMARY

A glass with high electrical conductivity, in addition to being of theoretical interest, would undoubtedly have many practical applications. It is the object of this investigation to attempt to improve the conductivity of glass by a systematic variation of composition. The components of the glass are compared on the basis of ionic size, valence and/or position in the periodic table as being a fundamental approach. Because of the preliminary nature of this phase of the investigation and in order to lay groundwork for more extensive study, modifications in composition include the following ions, many of which are reported in the literature:

Lithium	Barium
Sodium	Phosphorus
Potassium	Aluminum
Magnesium	Boron
Calcium	Tin

Silicate glasses were made in the form of standard discs from smelts of a few compositions using the above ions in the oxide form. The compositions, in addition to being restricted to two and three oxide systems, were altered by batch addition only. No attempt was made to change composition by an electrolytic process in the glass due to the scope of the investigation.

Conductivity measurements were made at room temperature using a megohm bridge. Although dielectric absorption was observed during measurements, no detailed study of this phenomenon was made because of the small effect it had on the conductivity.

## II. CONCLUSIONS

In addition to confirmation of the effects of various ions on electrical conductivity, as reported in the literature, the following trends were observed:

1. The sodium ion is more effective than either the lithium or potassium ion in increasing the electrical conductivity in a glass; the substitutions for each other being on a molar basis.

2. All the other oxides when substituted in a glass at the expense of silica tended to decrease the conductivity with the exception of alumina and tin. Alumina gave only a slight increase while tin oxide gave a significant increase in electrical conductivity.

## III. RECOMMENDATIONS

Because the limited amount of data obtained prevents making decisive conclusions, the following work is suggested:

1. Since tin showed the greatest promise in increasing conductivity, a more thorough study of its effects should be made.

2. In an effort to replace a large ion like potassium by a smaller one such as sodium in a glass and at the same time preserve the structure of the network, an electrolytic replacement could be tried. Methods of this process are described in the literature, but apparently little has been done with increasing conductivity as the objective.

3. Due to the limited amount of work which has been done on replacement of various ions by other ions either wholly or as combinations in a glass, on a molar basis, more effort in this direction would add fundamental interest and information to the over-all picture.

4. While the effects of dielectric absorption on the conductivity in a glass may be small, a thorough study of the phenomenon should shed light on the conduction process; thus significant ideas of approach would, possibly, be suggested.

#### IV. INTRODUCTION

The purpose of this investigation is to improve the electrical conducting properties of a glass. This work is undertaken not only in the interest of a more basic understanding of the structure of glass and its conduction processes, but as an effort to determine if a glass with highly conducting properties can be made for practical uses.

No attempt is made to exhaust all the possibilities in the work, but merely to verify methods and techniques; and to indicate trends not covered extensively by the literature.

#### V. REVIEW OF LITERATURE

To be able to explain the conduction process in glass, it is necessary to have some knowledge of the basic structure. Much has been written in the literature on the properties of glass. However, the major portion of the writings are of an empirical nature and deal with specific problems. For this reason, the theories of Zachariasen<sup>1</sup> seem to be the most plausible from a fundamental point of view.

Zachariasen frankly admits that we know very little concerning the atomic arrangement in glass. However, by making comparisons with the properties of crystals, he is able to arrive at extremely logical conclusions. Over large ranges of temperature, the mechanical properties of glass are comparable to those of crystals. For this reason, it seems logical to assume

that the forces linking the atoms together in the two forms of matter are essentially the same. Likewise, both form extended three dimensional networks. A discrepancy arises, from x-ray diffraction data, in that the network in glass is not periodic and symmetrical as in crystals. Yet it is not entirely random due to the fact that the internuclear distances do not sink below a given minimum value. Because of the lack of periodicity no two atoms are structurally equivalent in glass, while in crystals the reverse is true. The character of glass is thus isotropic and since all atoms are structurally unequivalent, the energy required to detach an atom from the network will be different for each individual atom. With increasing temperature we would therefore expect to get an increasing number of detached atoms, so that the breakdown of the network would be a continuous rather than an abrupt phenomenon. Migration of the detached atoms at a given temperature would occur and it is impossible to say at which temperature a given glass passes from the solid to the liquid state. Conversely, since the atoms in a crystal are structurally equivalent, as soon as the thermal energy reaches a definite value, all the equivalent atoms will be detached simultaneously; the crystal network breaks down abruptly and we get a definite melting point.

Glasses cannot be expressed as simple chemical compounds. The unit cell is infinitely large and consequently there will be no restrictions with regard to the relative numbers of chemically different atoms except that the valences must be balanced.

Of all the possible oxides only a very few are able to form glass.  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$  readily form glasses but all attempts to form  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  glasses have been in vain. No precise explanation of the ability to form



glasses of the oxides has been given. Zachariasen<sup>1</sup> has given Goldschmidt's attempt at correlating the ability to form glass with the value of the radius ratio  $R_A/R_O$  for oxides  $A_mO_n$ . Goldschmidt found that the radius ratio for all the oxides which have been prepared in vitreous form is around 0.2-0.4. This ratio corresponds to a tetrahedral arrangement of oxygen atoms around atom A, and he therefore believes that tetrahedral configuration is necessary for the formation of glass. However, the converse statement cannot be made: that an oxide with a radius ratio of about 0.3 will form a glass. Therefore, the conditions for the formation of glass are more complicated.

Because of the similarity of glasses and crystals and their difference as mentioned above, we may conclude that the energy of a glass will tend to run higher than that of a corresponding crystal. This is borne out by the fact that glasses show a more or less tendency to devitrify. Glasses which do not devitrify very rapidly will have an energy only slightly greater than that of the crystal. Zachariasen<sup>1</sup> thus expresses the ultimate condition for the formation of a glass: "The substance can form extended three-dimensional networks lacking periodicity with an energy content comparable with that of the corresponding crystal network.

In the crystalline forms of the oxides it is found that the oxygen atoms form polyhedra of one kind or another around atom A. If the energy of a glass is to be comparable with that of the crystal, the oxygen polyhedra in glass and crystal are essentially the same. In vitreous  $SiO_2$  we must, for example, expect to find tetrahedra of oxygen atoms around silicon. If the silicon were surrounded by any other number of atoms of oxygen, say three or five, the potential energy would be much greater and our energy requirement would not be met.

The linking together of the oxygen polyhedra in crystal lattices is done in such a way that no two atoms are in close contact. From an ionic viewpoint, we would expect a cation to be surrounded by as many anions as possible and vice versa. The upper limit of the number would be determined by the requirement that anions should not be in contact with each other. Ions of the same sign tend to be as far apart from each other as possible. The network of glass must obey these principles. The oxygen tetrahedra share corners with each other in such a manner that an oxygen atom is linked to two silicon atoms. The orientation of two tetrahedra with a common center will not be the same as in a crystal, but may vary within rather wide limits. From the considerations some simple rules may be formulated for glass formation: (1) an oxygen atom is linked to not more than two atoms A; (2) the number of oxygen atoms surrounding atoms A must be small; (3) the oxygen polyhedra share corners with each other, not edges or faces; and (4) in a three dimensional network at least three corners in each oxygen polyhedron must be shared.

Oxides  $X_2O$  and  $XO$  do not satisfy these requirements under any conditions. Under certain conditions other oxides, however, will fit these rules. We find readily the requirements (1), (3) and (4) are satisfied by oxides:  $A_2O_3$  if the oxygen atoms form triangles around each atom A;  $AO_2$  and  $A_2O_5$  if the oxygen atoms form tetrahedra around each atom A;  $AO_3$ ,  $A_2O_7$ ,  $AO_4$  if the oxygen atoms form octahedra around each atom A;  $AO_4$  if the oxygen atoms form cubes around each atom A. Agreement with Rule 2 cannot easily be decided. However, as no oxide  $AO_3$ ,  $A_2O_7$  or  $AO_4$  has been reported to have been prepared in the vitreous state, we may take that as an indication that only oxygen triangles and tetrahedra agree with Rule 2.

Of trivalent cations only the  $B^{+3}$ ,  $As^{+3}$  and  $Sb^{+3}$  ions have been found within oxygen triangles in crystal lattices.  $P^{+3}$  is the possibility of another ion in this group. One important fact is worth mentioning. Whereas boron is lying in the plane of the three surrounding oxygen atoms, arsenic, antimony and probably phosphorus are displaced out of the plane. The configuration around the latter ions is, as a matter of fact, a hybrid between a triangular and octahedral configuration. In  $As_4O_6$  and  $Sb_4O_6$  there are six oxygen atoms around As or Sb, three of the oxygen atoms being closer to the cation than the rest. In  $As_4O_6$  the two distances are  $2.01\text{\AA}$  and  $2.78\text{\AA}$ ; in  $Sb_4O_6$  the two distances are more nearly equal, namely,  $2.22\text{\AA}$  and  $2.61\text{\AA}$ . The approximation to the coordination number three is thus closer for  $As^{+3}$  than for  $Sb^{+3}$ , and we must expect that for  $P^{+3}$  the approximation is still closer than for  $As^{+3}$ .

In the series  $P_2O_3$ ,  $As_2O_3$ ,  $Sb_2O_3$  the ability to form glass therefore will decrease in the order given.  $B_2O_3$ , however, should form glass with greater ease than any other oxide. No other sesquioxide than the four given can be expected in the vitreous form.

Of the quadrivalent cations only  $Si^{+4}$  and  $Ge^{+4}$  are surrounded by oxygen tetrahedra in crystal lattices.  $SiO_2$  and  $GeO_2$  consequently may occur in the vitreous state. The ability to form glass will be less than for  $B_2O_3$  because of the greater coordination number.

The pentavalent cations  $P^{+5}$  and  $As^{+5}$  are always surrounded by oxygen tetrahedra, probably also  $V^{+5}$ . It is possible that also  $Sb^{+5}$ ,  $Cb^{+5}$  and  $Ta^{+5}$ , may occur with coordination number four with respect to oxygen. The available crystal structure data are, however, too few to allow definite conclusions.

Extending the argument to fluorides, Zachariasen<sup>1</sup> concludes that  $\text{BeF}_2$  is the only fluoride which can be expected to form glass and is in complete agreement with observations.

The above discussion applies when a single oxide is considered. In oxide glasses of a general nature the circumstances are much more complicated. Therefore the rules for the individual oxides must be modified; an oxide glass may be formed (1) if the sample contains a high percentage of cations which are surrounded by oxygen tetrahedra or by oxygen triangles, (2) if these tetrahedra or triangles share only corners with each other and (3) if some oxygen atoms are linked to only two such cations and do not form further bonds with any other cations. This means that the glass must contain appreciable amounts of the cations which can form vitreous oxides or of other cations which are able to replace any of the former isomorphously. These glass-forming cations are  $\text{B}^{+3}$ ,  $\text{Si}^{+4}$ ,  $\text{P}^{+3}$ ,  $\text{P}^{+5}$ ,  $\text{As}^{+3}$ ,  $\text{As}^{+5}$ ,  $\text{Ge}^{+4}$  and possibly  $\text{V}^{+5}$ ,  $\text{Sb}^{+5}$ ,  $\text{Cb}^{+5}$ ,  $\text{Ta}^{+5}$  and in addition  $\text{Al}^{+3}$ , which is capable of replacing  $\text{Si}^{+4}$  isomorphously, except  $\text{Al}_2\text{O}_3$  alone cannot form a glass.

The chemical composition of a glass can be expressed by a gross "chemical formula" of the form  $\text{A}_m \text{B}_n \text{O}$ . In this "formula"  $m$  and  $n$  are not necessarily integers but merely represent the number of atoms of A and B per oxygen atom. Cations B are the glass forming ones listed above, while all others are grouped under A. For a tetrahedral glass the value of  $n$  in the gross formula will lie between 0.33 and 0.50. For a triangular glass it will be 0.67.

When a three-dimensional framework of oxygen atoms and atoms B are built up, the valences will in general not be balanced, so that additional cations must be introduced. Because the oxygen polyhedra in this framework

are tetrahedra or triangles, holes necessarily must exist in the network. These holes will be bounded by oxygen atoms, so that they are excellently suited as positions for the cations A. Also, since the framework itself is without periodicity and symmetry the holes must be statistically distributed and there will be no restriction on behalf of symmetry as to which and how many of these holes are to be filled by cations A. In agreement with previous results this shows that the chemical composition cannot be expressed by a rational chemical formula. Some statements are made as to the nature of atoms A. A requirement is that the introduction of atoms A into the framework does not cause great increase of the potential energy. The fact that the cations A go into the holes is in agreement with that requirement. The holes are being filled as the framework is being formed and the dimensions of the holes are determined by the size of the cations occupying them. The cations A and B exert repulsive potentials against each other which must be small. The holes are to a great extent bounded by edges of the oxygen triangles or tetrahedral faces and the cations B carry charges 3, 4 or 5. In order to make the repulsion between cations A and B small, the charge on cation A must be small and the distance between cations large. The distance is increased if the holes are enlarged which can only be brought about if the cations A are large. Small and highly charged cations like  $Ti^{+4}$ ,  $Mg^{+2}$  will tend to produce devitrification. Typical A cations in glasses are  $Na^+$ ,  $K^+$ ,  $Ca^{+2}$ ,  $Ba^{+2}$ ,  $Pb^{+2}$ .

Some conclusions regarding the relationship of composition and properties are:

1. The rigidity which glasses possess over ranges of temperature indicates no appreciable migration of the atoms occurs at relatively low

temperatures.

2. Cations A, especially alkalis, will be bound less tightly to the oxygen atoms than cations B. Thus as the temperature rises we must expect to get an increasing number of migrating atoms A, without any appreciable breakdown of the vitreous framework proper.

3. Univalent cations will migrate with greater ease through the framework than the divalent cations, and again smaller cations will migrate more easily than large cations with the same charge. Thus  $\text{Na}^+$  migrates more easily than  $\text{K}^+$ , while both will migrate more readily than  $\text{Ca}^{+2}$ .

4. The electrical conductivity of a glass must be chiefly electrolytic, the charge being carried by cations and for the most part by the alkali ions.

5. Owing to the increasing number of detached atoms with increasing temperature, the conductivity will also increase with temperature.

6. At higher temperatures breakdown of the vitreous framework proper will begin, and large parts of the framework may start migrating. Even in the melt oxygen atoms and atoms B to a very great extent are linked together so as to form rather large groups, the degree of polymerization being a function of the temperature. In melts where such highly associated groups occur, the viscosity will be high.

7. Whether a substance will form a glass depends to a large degree on cooling conditions. Previously we had considered whether a substance could form a glass.

Morey<sup>2</sup> describes the process of conduction of electricity in glass as an electrolytic process depending on the temperature, the composition and the surrounding conditions. Since the present work described in this paper

relates to the effect of composition, the temperature and surrounding conditions are held constant within feasible limits. Volume conductivity is expressed as the reciprocal of volume resistivity. This in turn may be defined as the longitudinal resistance in ohms per unit of length of a uniform bar of unit sectional area.

The extensive measurements of Fulda as described by Morey<sup>2</sup> give resistivities of glasses as a function of composition. These measurements indicate that the alkali ions make the greatest contribution to conductivity, the effect of sodium being more than that of potassium, the larger ion. Fulda's work indicated that replacement of  $\text{SiO}_2$  by ions of calcium, barium, lead, magnesium and zinc decreased the conductivity; the effect being greatest with calcium and least with zinc. Boron as  $\text{B}_2\text{O}_3$  decreased the conductivity while aluminum as  $\text{Al}_2\text{O}_3$  increased the conductivity when each were substituted in a  $\text{Na}_2\text{O-SiO}_2$  glass at the expense of  $\text{SiO}_2$ .

Much of the work which has been done on the conductivity of glass has been confined to arbitrary excursions into three component systems. Additional components usually have unpredictable results. The published literature is highly empirical in nature and, no doubt due to the complexity of a system, very little is given to quantitative explanation.

## VI. PROCEDURE

A. Source of raw materials.

Due to the unknown effects which might be introduced from impurities in the materials, chemically pure compounds were used as sources of the various ions. The following is a list of the compounds used:

Anhydrous lithium carbonate  
Anhydrous sodium carbonate  
Anhydrous potassium carbonate  
Anhydrous calcium carbonate  
Anhydrous magnesium carbonate  
Anhydrous barium carbonate  
Ignited aluminum Oxide  
Phosphoric acid ( $P_2O_5$ ), anhydride  
Boric acid  
Tin oxide ( $SnO_2$ )  
Ottawa sand (99.89%  $SiO_2$ )

B. Preparation of glass batches.

Raw materials were weighed to an accuracy of  $0.1 \pm 0.05$  grams in 100 gram batches. These batches were mixed by hand using a camels-hair brush for approximately fifteen minutes, then introduced into a platinum -10% rhodium crucible in small portions for smelting. The smelting furnace was a globalar type employing silicon carbide heating elements. This was necessary in order to obtain a still air atmosphere. The furnace was preheated to a temperature of  $1200^\circ C$  for smelting. Precaution had to be taken in keeping the level of the batch well below the top of the crucible to pre-



vent overflow until the smelt was complete. This was due to the volatile carbon dioxide in the carbonates and water in the boric acid.

The batches were smelted for a period of five hours and poured on a steel slab. After cooling, the batches were crushed to approximately 50 mesh and resmelted for another period of five hours. This procedure was adopted to insure homogeneity of the sample. The smelting temperatures varied to some degree ( $1200 \pm 100^{\circ}\text{C}$ ) the criterion being to obtain a good pouring consistency. After the second smelt, each sample was checked for homogeneity by index of refraction matching in a representative sample.

C. Preparation of specimens for conductivity measurement.

Specimens were poured from the second smelt into a steel mold two inches in diameter by  $3/16$  inch deep. The mold had been coated with graphite and slightly heated to prevent sticking and too rapid cooling of the specimen. The samples were immediately introduced into a small kanthal-wound resistance furnace which had been preheated to  $400^{\circ}\text{C}$ . After a time of the order of one hour was allowed for the samples to attain an equilibrium condition, the furnace was turned off and the specimens were permitted to cool to room temperature overnight. This represents a cooling rate of approximately  $25^{\circ}\text{C/hr}$ . This annealing procedure was adopted not only to relieve the mechanical strains in the glass, but to hold constant so far as possible the thermal history. Variations in annealing are held to have significant influences on the electrical conductivity.

The samples were ground to a thickness of approximately  $0.175''$  and polished to a high luster using a B. & I. Manufacturing Company gem maker. Silver electrodes  $1.5''$  in diameter were painted on either side of the specimen with DuPont's No. 4760 silver paint. After drying at  $110^{\circ}\text{C}$

for 24 hours, the samples were stored in a desiccator for measurement.

#### D. Measurement of conductivity.

Samples were removed singularly from the desiccator after cooling to room temperature and measurements of resistance using a General Radio type 544-B megohm bridge were taken. This unit measures resistances of the same order of magnitude as the resistances of the samples of this investigation with an accuracy of  $\pm 3\%$ . Since some capacitance was introduced in parallel with the resistance of the sample due to specimen geometry, dielectric absorption was encountered. The resistance was found to change by factors of one-third or less with time of measurement to approximately a constant value. This, in turn, would depend on the time constant  $RC$  of the sample where  $R$  is the pure resistance and  $C$  is the capacitance. No detailed study of this phenomenon was attempted at this time.

### VII. RESULTS

Resistivities were calculated according to the formula:

$$\rho = R \frac{A}{t} \text{ where } R \text{ is the resistance in ohms.}$$

$A$  is the area of cross-section in  $\text{cm}^2$ .

$t$  is the thickness in cm.

$\rho$  is thus the resistivity in ohm-cm.

The conductivity is equal to  $\frac{1}{\rho}$  and is expressed in  $\text{mho-cm.}^{-1}$  Table 1 gives percentage of composition by weight and conductivity calculations.

The values of conductivity represent the average of two specimens fabricated from each smelt. Each specimen varied approximately 2% to 3% from the mean which is of the same order of magnitude as the error in measurement of resistance using the megohm bridge. Other tables and figures give data where a comparison of various effects may be made.

TABLE I

## GENERAL COMPOSITION AND CONDUCTIVITY DATA

Spec. No.	Percentage composition by weight											Conductivity $\text{mho-cm}^{-1}$
	$\text{Li}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{MgO}$	$\text{CaO}$	$\text{BaO}$	$\text{B}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{P}_2\text{O}_5$	$\text{SnO}_2$	$\text{SiO}_2$	
C-4		20			10						70	$8.3 \times 10^{-12}$
C-1		30			10						60	$3.2 \times 10^{-10}$
C-2		40			10						50	$3.5 \times 10^{-9}$
C-3		50			10						40	No glass
C-6		40			5						55	$1.4 \times 10^{-9}$
C-7		40									60	$4.7 \times 10^{-8}$
C-5			40		10						50	$2.0 \times 10^{-10}$
C-8			40								60	$3.9 \times 10^{-10}$
C-13			50.3								49.7	Hygroscopic
C-12	40										60	No glass
C-14	24.3										75.7	$2.9 \times 10^{-9}$
C-22		24.3									75.7	$2.8 \times 10^{-9}$
C-19		40		10							50	$7.9 \times 10^{-9}$
C-18		40				10					50	$1.4 \times 10^{-8}$
C-9		40						5			55	$5.5 \times 10^{-8}$
C-10		40						10			50	$5.1 \times 10^{-8}$
C-11		40						15			45	$6.5 \times 10^{-8}$
C-16		40					10				50	$3.4 \times 10^{-8}$
C-17		40					20				40	$2.0 \times 10^{-8}$
C-20		40							10		50	$2.6 \times 10^{-8}$
C-21		40								10	50	$1.5 \times 10^{-7}$

TABLE II

COMPOSITION AND CONDUCTIVITY DATA FOR  $\text{Na}_2\text{O} - \text{CaO} - \text{SiO}_2$  GLASS

Spec. No.	Percentage composition by weight			Conductivity $\text{mho-cm}^{-1}$
	$\text{Na}_2\text{O}$	$\text{CaO}$	$\text{SiO}_2$	
C-4	20	10	70	$8.3 \times 10^{-12}$
C-1	30	10	60	$3.2 \times 10^{-10}$
C-2	40	10	50	$3.5 \times 10^{-9}$
C-3	50	10	40	No glass

TABLE III

DATA FOR COMPARISON OF EFFECT OF  $\text{Na}_2\text{O}$  AND  $\text{K}_2\text{O}$  ON CONDUCTIVITY

Spec. No.	Percentage composition by weight				Conductivity $\text{mho-cm}^{-1}$
	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{SiO}_2$	
C-5		40	10	50	$2.0 \times 10^{-10}$
C-2	40		10	50	$3.5 \times 10^{-9}$
C-8		40		60	$3.9 \times 10^{-10}$
C-7	40			60	$4.7 \times 10^{-8}$
C-13		50.3		49.7	Hygroscopic
C-15	30.5			69.5	$4.9 \times 10^{-9}$

TABLE IV

DATA FOR COMPARISON OF EFFECT OF  $\text{Na}_2\text{O}$  AND  $\text{Li}_2\text{O}$  ON CONDUCTIVITY

Spec. No.	Percentage composition by weight			Conductivity $\text{mho-cm}^{-1}$
	$\text{Na}_2\text{O}$	$\text{Li}_2\text{O}$	$\text{SiO}_2$	
C-12		40	60	No glass
C-7	40		60	$4.7 \times 10^{-8}$
C-14		24.3	75.7	$2.9 \times 10^{-9}$
C-22	24.3		75.7	$2.8 \times 10^{-9}$

Fig. 1

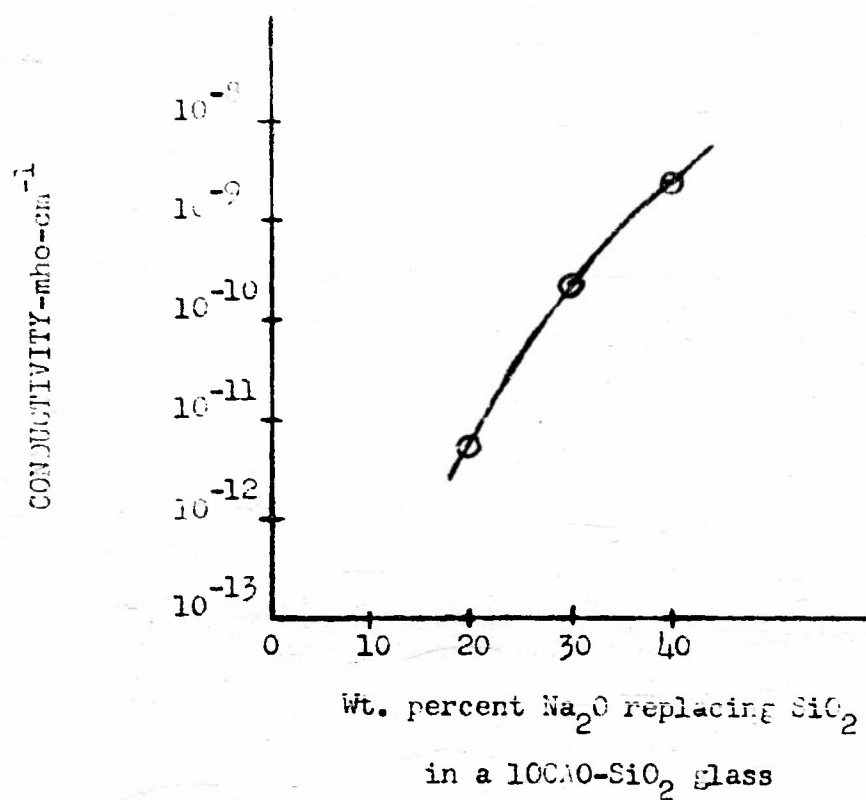


Fig. 2

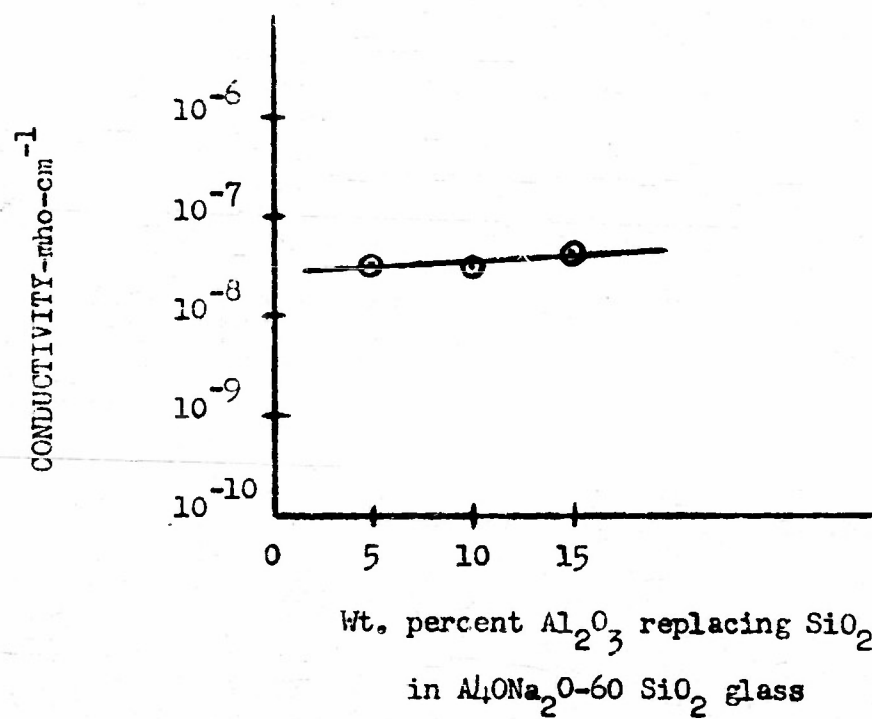


TABLE V

## DATA FOR ALKALINE EARTH GLASSES

Spec. No.	Percentage composition by weight					Conductivity mho-cm <sup>-1</sup>
	Na <sub>2</sub> O	CaO	MgO	BaO	SiO <sub>2</sub>	
C-2	40	10			50	$3.5 \times 10^{-9}$
C-19	40		10		50	$7.9 \times 10^{-9}$
C-18	40			10	50	$1.4 \times 10^{-8}$
C-7	40				60	$4.7 \times 10^{-8}$

TABLE VI

## CONDUCTIVITY DATA FOR MISCELLANEOUS OXIDES SUBSTITUTED IN A SODIUM-SILICATE GLASS

Spec. No.	Percentage composition by weight						Conductivity mho-cm <sup>-1</sup>
	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SnO <sub>2</sub>	SiO <sub>2</sub>	
C-7	40					60	$4.7 \times 10^{-8}$
C-9	40	5				55	$5.5 \times 10^{-8}$
C-10	40	10				50	$5.1 \times 10^{-8}$
C-11	40	15				45	$6.5 \times 10^{-8}$
C-16	40		10			50	$3.4 \times 10^{-8}$
C-17	40		20			40	$2.0 \times 10^{-8}$
C-20	40			10		50	$2.6 \times 10^{-8}$
C-21	40				10	50	$1.5 \times 10^{-7}$

Fig. 3

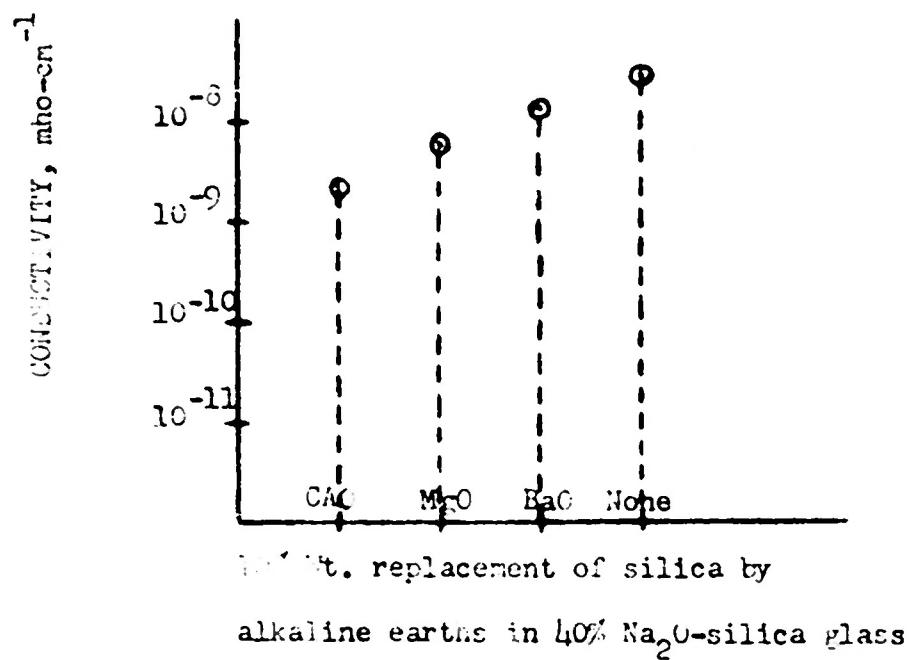
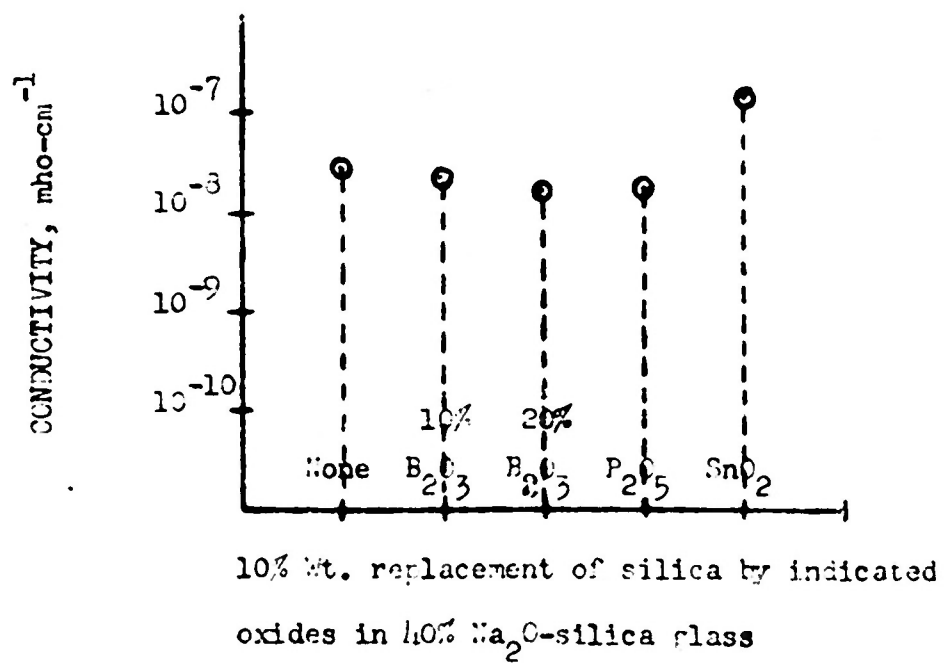


Fig. 4



## VIII. DISCUSSION OF RESULTS

A comparison of glasses C-1, C-2 and C-4 in Table II indicates that the conductivity increases as the alkali content is increased at the expense of  $\text{SiO}_2$ . Composition C-3 would not form a glass with the  $\text{SiO}_2$  content as low as 40% in this system. This composition crystallized indicating the formation of a definite periodic and symmetrical network not found in true glasses.

Composition C-5 as compared with C-2 as well as C-8 as compared with C-7 in Table III shows the smaller sodium ion to be more effective in promoting conductivity than the larger potassium ion. The effect is more pronounced in the latter two glasses, possibly due to the role played by the calcium in the former to give a counter-effect. Composition C-15 was made for a comparison of sodium and potassium on a molar basis. A comparison of this glass with C-8, both representing alkali-2.35  $\text{SiO}_2$  molar composition again shows the sodium ion making the greatest contribution to conductivity. In an effort to make a comparison of potassium with sodium in a molar substitution of the composition of C-7, namely alkali-1.55  $\text{SiO}_2$  glass C-13 was made. This glass was so hygroscopic that it formed a liquid potassium-silicate after setting overnight in air.

No comparison on the substitution of  $\text{Li}_2\text{O}$  for  $\text{Na}_2\text{O}$  in composition C-7 could be made in that composition C-12 would not form a glass. This is in accordance with the work of Kracek<sup>3</sup> who found that only mixtures containing more than 70%  $\text{SiO}_2$  could be obtained in the form of fairly stable glasses. As a consequence of this difficulty, compositions C-14, and C-22 were made as a basis for comparison. C-14 represents the same molar composition as C-7. As shown in Table IV the  $\text{Na}_2\text{O}$  is more effective than  $\text{Li}_2\text{O}$  on this basis. There is very little difference in the conductivity of C-14



and C-22, which are the same on a weight basis. However, C-22 represents a molar composition of  $\text{Na}_2\text{O}-3.22 \text{ SiO}_2$  while C-14 represents a molar composition of  $\text{Li}_2\text{O}-1.55 \text{ SiO}_2$ . Thus again  $\text{Na}_2\text{O}$  is more effective than  $\text{Li}_2\text{O}$  in increasing the conductivity. This may be explained by the fact that lithium holds a unique position in the periodic table and forms silicates intermediate in position between those of the alkalis and the alkaline earths.

All of the alkaline earths  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{BaO}$ , as is shown in Table V, decreased the conductivity when substituted at the expense of  $\text{SiO}_2$ . This may be seen by comparing compositions C-2, C-7, C-18, and C-19. The effect of  $\text{CaO}$  was the greatest and that of  $\text{BaO}$  the least in this respect. Apparently these compounds play an intermediate role in the make-up of the glass, that being to modify the structure itself as well as to contribute to the conductivity. The order of increasing size of these ions is magnesium, calcium and barium respectively. Thus no conclusion can be drawn from so limited an amount of investigation as to size of ion. It is possible that barium being much the heavier and larger of the group plays some part with the  $\text{SiO}_2$  in opening up the network for the migration of the sodium ion.

The substitution of phosphorus as  $\text{P}_2\text{O}_5$  at the expense of  $\text{SiO}_2$  in C-7 gave a slight decrease in conductivity as is evidenced in C-20. While  $\text{Al}_2\text{O}_3$  yielded a slight increase in conductivity,  $\text{B}_2\text{O}_3$  had the reverse effect as indicated by a comparison of C-7 with C-9, C-10, C-11, C-16 and C-17. All these results are shown in Table VI.

Because of the metallic properties of tin and its being in the

same group as silica in the periodic table, composition C-21 was made to get some indication of its effect when substituted in C-7 at the expense of  $\text{SiO}_2$ . The highest conducting glass of all the compositions tried was obtained, increasing the conductivity of C-7 by a factor of three or more. Interesting and no doubt enlightening results might be obtained by further research in this direction.

The results obtained in this investigation, although not so extensive as those of Fulda as described by Morey<sup>2</sup>, agree favorably with Fulda's work. Excellent agreement with the theories discussed in the literature by Zachariasen<sup>1</sup> is noted.

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